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CHAPTER 4
LABORATORY INVESTIGATIONS

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1.0 INTRODUCTION

Laboratory studies related to cometary grains and the nuclei of comets can be broken down into three areas which relate to understanding the spectral properties, the formation mechanisms, and the evolution of grains and nuclei:

1) Spectral studies to be used in the interpretation of cometary spectra,

2) Sample preparation experiments which may shed light on the physical nature and history of cometary grains and nuclei by exploring the effects on grain emissivities resulting from the ways in which the samples are created, and

3) Grain processing experiments which should provide insight on the interaction of cometary grains with the environment in the immediate vicinity of the cometary nucleus as the comet travels from the Oort Cloud through perihelion, and perhaps even suggestions regarding the relationship between interstellar grains and cometary matter.

This summary will present a rather different view of laboratory experiments than is usually found in the literature, concentrating on measurement techniques and sample preparations especially relevant to cometary dust. In addition, it attempts to assimilate the information provided in B. Donn's talk at the workshop, some of his excellent, comprehensive references (Donn, 1985 and 1987), and the informal presentations by L. Allamandola, R. Thompson, T. Mukai, and the author. Another recent general overview of interstellar dust questions may be found in Tielens and Allamandola (1986). Extended abstracts of presentations made in this session are included in the Appendix.

Based on over two hours of animated discussion by the laboratory investigations working group on 10 August and numerous comments throughout the workshop, several areas of study were endorsed as important for furthering our understanding of cometary grains and nuclei. Some of these have been worked into the text in this chapter, and a summary of these recommendations is included in Chapter 5.

Laboratory studies of interplanetary dust particles were also recognized as important for our understanding of cometary dust. These particles were discussed in Session III and thus are not treated here (see paper by Walker, Chapter 3).

2.0 SPECTRAL STUDIES

Studies of infrared spectra of simulated cometary grains can lead to the identification of materials present in comets, shed light on the physical state and thermal history of the grain material using details of emission band structure, and aid the development of analytical treatments for predicting the emissivities of small particles near resonances in the optical constants of corresponding bulk samples. These studies can also be useful in planning future comet observations and instruments, for example, in the selection of spectral filters for CRAF and earth-orbiting instruments, by predicting where new spectral features may exist or elucidating what bandpasses would best improve our understanding of known features, and defining the spectral resolution necessary to resolve such band structures. This workshop focused on the mineral phase (primarily silicates) and hydrocarbons, but

ices and gas phase molecules (especially those such as CN which were shown to have been released by "parent" grains at a range of distances from the nucleus of Halley's Comet) are also important subjects of IR spectroscopic studies.

Spectral studies have been basically of three types; reflectance, transmittance, and emittance, and these are discussed in turn.

2.1 Reflectance

Reflectance measurements from polished surfaces can be used to derive optical constants of bulk samples. The optical constants can, in principle, be used to compute spectral emissivities of grains of the same precise composition as the bulk material but of arbitrary size, shape, and physical properties. However, as pointed out in Chapter 2, a comprehensive analytical treatment for the calculation of the scattering and emissivity as a function of wavelength for irregular, inhomogeneous particles is lacking. Thus, a complementary and perhaps more straightforward approach is to study the spectra of particulate samples which have some similarity to cometary grains, bearing in mind that particle size and shape, temperature, surface roughness, and even degree of aggregation of spherical particle samples ALL affect the resulting wavelength dependence of emissivity and scattering. Thus, this session focused on transmission and emission, and for a more complete discussion of optical constants we refer the reader to Chapter 2.

However, spectral reflectance studies (in some cases combined with transmission work) still seem to have a lot to offer in the study of thin films, such as those sputtered onto a surface (Day 1979 and 1980) or deposited onto a surface at low temperature. In both of these situations one attempts to measure spectral structure by reflectance not from a polished surface, but rather from an aggregate of material which, in practice, is likely to be a continuous, fairly smooth surface (although the surfaces so studied were not examined by SEM). Thin films are particularly useful for obtaining the spectra of volatiles or residues from processing of simple ices. In practice, this may be a reasonable way to create an analog for a cometary nuclear surface, but it has a limited application to the study of emitting and scattering particles seen in the visible and infrared.

Clearly, scattering from a single particle is an extreme case of reflectance. While one would ideally like to measure infrared scattering and emissivity of suspended, individual particles (preferably in a vacuum), relatively few studies of this type have been done at any wavelength (e.g., Ashkin 1970, Ashkin and Dziedzic 1971 and 1980, Hecht 1979a, b; Philip *et al.*, 1983; Marx and Mulholland 1983, and Arnold *et al.* 1982 and 1984) and can be prohibitively difficult experimentally. For example, it is very difficult to obtain single particles of volatiles, although they can be prepared as thin films or sputtered layers with comparative ease. The flux from a single particle at infrared or shorter wavelengths, especially at large scattering angles, is small and thus hard to measure. The forward scattering component can be lost in the incident (unscattered) flux.

One approach to investigating the scattering by single particles is to scale both particle dimensions and wavelength to the microwave region. Materials then have to be found with microwave optical constants matching those of interest for cometary grains at shorter wavelengths.

Two groups are pursuing this technique with application to astronomical grains. One group is now at the University of Florida (Schuerman 1980) the other is at the Ruhr University, Bochum FRG (Zerull *et al.* 1980). These facilities are valuable for studying effects of shape and roughness on the optical scattering. However, these experiments are not designed to derive emissivity functions so critical to compositional analysis based on infrared spectroscopy of cometary comae.

Weiss-Wrana (1983) suspended single particles electrostatically and measured the angular scattering of various silicate, carbonaceous, and meteoritic particles with a laser. Giese *et al.* (1986) have extended these measurements to three wavelengths. Some IDPs

have been studied by using advanced methods for thin sectioning in a support medium and clever optical enhancement techniques, but these experiments don't even attempt to simulate free particles in space.

Although some progress in this direction (which would even include zero g conditions) may be possible on the space station, we must push ahead in terrestrial labs now. Thus, measurements of ice films and residues, organic residues, and sputtered refractory films represent one of the active, productive areas of laboratory simulation going on today. Several groups (see below) are exploring the properties of ices and ice residues after a variety of methods of processing the films has been applied.

2.2 Transmittance

Perhaps the most abundant source of astrophysically relevant spectral information is the vast array of transmission measurements conducted on laboratory, lunar, terrestrial mineral, and meteorite samples, and even interplanetary dust particles. Because of the relative ease with which a sample can be put into a lab spectrometer and transmission (or more precisely, extinction = absorption + scattering) obtained, this has been a very productive survey technique. Good, comprehensive reference examples for minerals, etc., include, but by no means are limited to, Ferraro (1982), Hunt, Wisherd, and Bonham (1950), and Nyquist and Kagel (1971), and for IDPs, Sandford, Fraundorf, Patel, and Walker (1982), Sandford and Walker (1985), and Sandford (1985). A word of caution: One must be concerned about the fact that transmission data usually include the extinction due to scattering as well as the absorption which is of interest in the analysis of astronomical emission spectra. However, as was pointed out by Gehrz and Huffman, a further complication is that for some small lab instruments some of the radiation scattered out of the beam may still be detected if the sample and the light collector (or detector) are close enough together.

Even though one cannot be confident that all or none of the scattering effects are being measured, the technique is still very valuable for associating certain spectral features with specific groups, radicals, etc. in the samples. We simply point out that one can be misled in using pellet transmission spectra to identify the materials causing an emission spectrum, as the scattering wings on the sides of strong resonant features can make the features look very different from those seen in emission where only the absorption component of the transmission really applies.

To date, most of the transmission data have been obtained with "standard" lab instruments, such as those made commercially by Beckman and Perkin-Elmer. Recently, Fourier Transform interferometers for the IR (FTIRs) have become much more common, and machines by Nicolet and Mattson have permitted the computer controlled automatic acquisition of entire spectra from about 2.5μm to 25 or 40μm. The use of the computer permits easy averaging of many spectra with the ability to print out the results in digital as well as graphic form. Data are typically saved on disk, and post-processing is frequently done. Few systems are currently used to acquire data beyond 40μm, and there are not that many used regularly beyond 25μm. The new devices have options allowing work all the way to the sub-millimeter, but these capabilities have not been exploited in lab studies such as we are discussing here.

The emissivity technique to be discussed below would allow the use of the same long wavelength spectrometers in the laboratory as are used for the astronomical observations. In principle, detectors from these spectrometers could also be used for transmission studies, as several of the new FTIR machines allow the user to provide the detector, and the output of the detector is fed into the computer that takes the interferogram and controls the mirror. The entire spectrometer could be used with more difficulty in conjunction with a Beckman or P-E, but the sensitivity would likely be lower and the aggravation factor much higher. However, all of these experiments which use the *same* instrument to take the astronomical and laboratory data have the advantage of producing spectra that are

much easier to compare. In view of the expected increase in number, quality, and spectral resolution of cometary spectra, the workshop participants recognized the need for long wavelength lab studies ($\lambda > 50\mu$m, out to 200μm or beyond).

2.3 Emittance

A very promising technique, based on the response of several attendees and the success of earlier published studies, is the use of actual emissivity measurements. This technique was pioneered by Lyon (1964) and Hunt (1976), who showed that the emissivity of a collection of small grains resting on a polished metal surface (usually copper to insure a single, uniform temperature) was the same as that of the grains floating in a vacuum, except for the addition of the grain emission reflected by the metal back toward the detector and the (easily subtracted) low, featureless background due to the polished metal. Thus, if one desired only to obtain the spectral shape and not the absolute grain emissivity, the technique was clean and fairly simple to use.

Rose (1977) utilized this technique in his thesis work analyzing meteorite samples, studying lunar samples, and exploring simulated astronomical grains produced by aqueous condensation (Day, 1976b). His apparatus used a chopping primary mirror to modulate the sample signal and remove the infrared background. He showed that the emission from amorphous silicates provided a good match to the spectral shape emitted by astronomical grains that had not been subjected to significant heating. Grains that had been heated or created with lattice structure showed spectral peaks characteristic of the mineral composition, similar to transmission spectra but with typically narrower peaks and, in some instances, at slightly different wavelengths.

Stephens and Russell (1979) and Nuth and Donn (1982, 1983b and references therein) used the techniques of laser vaporization and smoke condensation respectively, to produce similar amorphous silicate particles about 200 A in size which stuck together in long, fractal-like chains and masses. The emissivity of such particles has been shown (Stephens and Russell 1979, and Cohen et al. 1980) to reproduce the shape and central wavelength of interstellar (Trapezium-like) silicate emission at *both* 10 and 20μm with a chi-squared per degree of freedom of 1-2, and to fit the broad, smooth 10μm feature in Comet Kohoutek

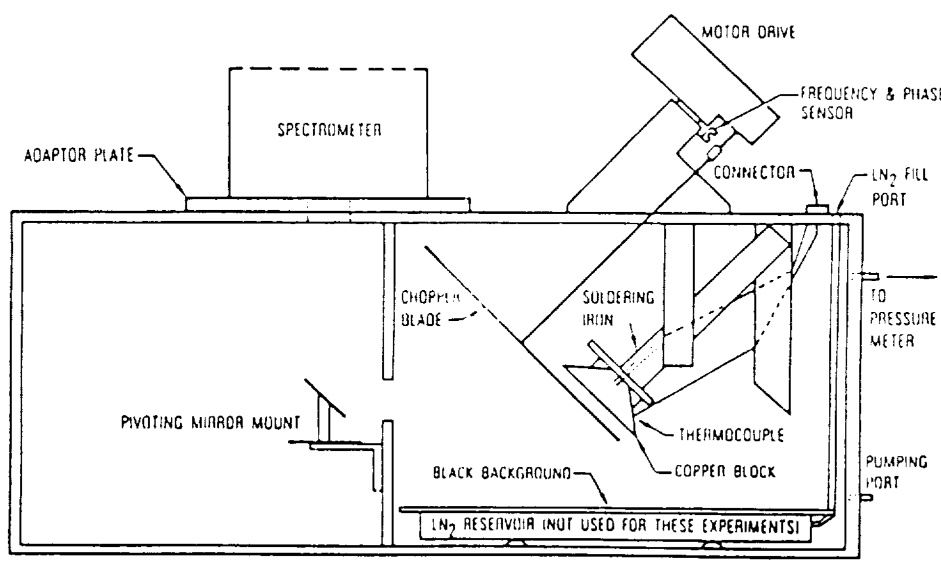

Figure 3.1 - Top schematic view of the emissivity chamber used to make the emission measurements. Sample typically covers $\leq 10\%$ of the surface of the copper block. The copper block is heated to either 42,77 or 127 C in making the mesurements (from Hecht *et al.* 1986).

as well. Moreover, it was pointed out by Huffman that the ground enstatite and olivine spectra in Stephens and Russell looked remarkably similar to the Halley spectrum shown by Campins at the Workshop. The successful use of this emission study to match the spectra, and thus explain the nature, of two astronomical dust populations suggests that emissivity measurements are a very promising avenue for investigating cometary grain composition.

The schematic of the chamber used by Stephens and Russell is shown in Figure 3.1 as a simple, inexpensive way of obtaining such data. Figure 3.2 shows some of the data obtained with the chamber using the same CVF instruments as were used to obtain the comet data. Again, as was noted above but bears repeating again, having lab data taken with the *same* instruments as were used for the cometary studies greatly facilitates a clean, unambiguous comparison of the spectra.

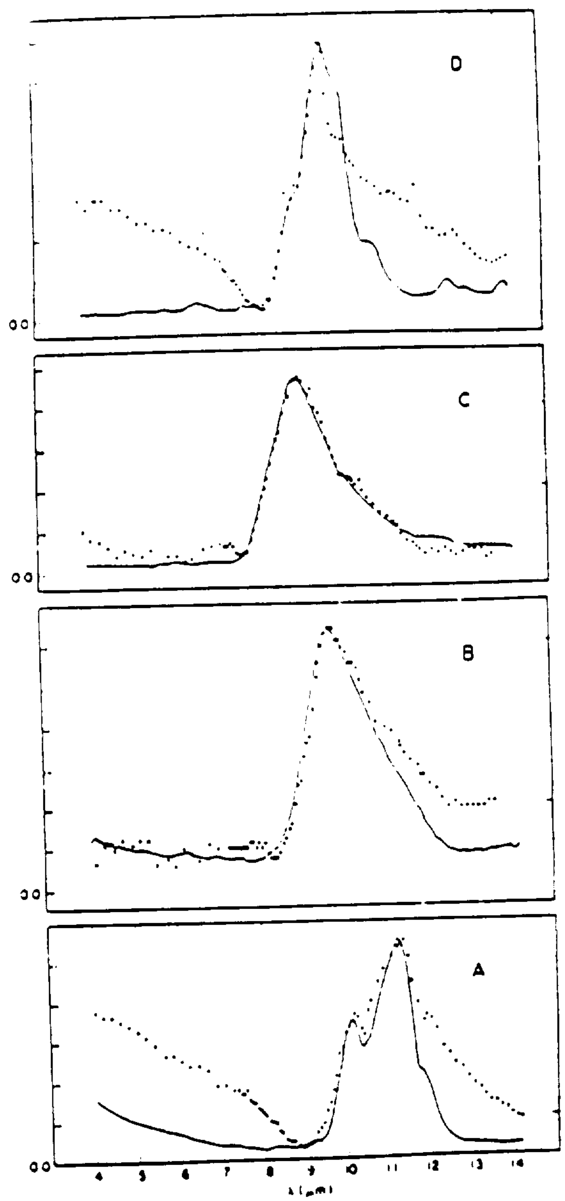

Figure 3.2 - Absorption (extinction spectra (*dots*) of A: ground olivine B: olivine condensate C: enstatite condensate; and D: ground enstatite, superposed on the corresponding emissivity data (*solid lines*) from Figure 3 (from Stephens and Russell 1979).

3.0 SAMPLE PREPARATION

In his recent review, "Experiments on the Formation, Properties and Processing of Cosmic Dust," Donn (1987) has provided a comprehensive reference list covering work on the physics and chemistry of working with dust samples which are designed to further our understanding of astronomical dust grains. Here, we will explore some of the practical considerations of producing collections of grains which we believe are related to those grains being observed by the "cometary spectroscopist," as well as some new lab efforts begun as a result of work on the identification of interstellar grains through infrared emission features.

3.1 Established Techniques for Producing and Studying Mineral Grains

Techniques for the preparation of cometary dust analogues include the grinding of mineral samples into micron or sub-micron size particles, deposition of dust samples on mirrored surfaces, condensation of smokes in an arc, condensation of laser-vaporized mineral material in a controlled atmosphere, pressing and grinding and re-pressing pellets (to get a uniform pellet sample), such as KBr, with a grain material present, collection of films both at warm temperatures and near 10 K , and collection of organic matter inside glass vessels with controlled atmospheres, just to name several. Each has inherent advantages and drawbacks, and thus the use of several approaches for the production of the same or similar samples probably gets us closest to the truth; deficiencies in each approach should become more apparent when the results, specifically the wavelength dependencies of the emissivity of the dust, from different experiments are compared.

An example familiar to the author of the added insight resulting from using two different experimental approaches relates to dust sample preparation via laser vaporization and condensation in a controlled atmosphere of a mineral sample of known composition (Stephens and Kothari 1978, Hecht *et al.* 1986) versus grinding up particles and pressing them in a KBr pellet versus using an arc to create a smoke. In the laser vaporization one can use a vast array of materials in different forms. The starting substance can be well characterized, and the atmosphere varied to simulate inert, O-rich, C-rich, or H-rich environments. However, as pointed out by Donn, the condensation is occurring at much higher densities than those found in astronomical situations, and we need to worry about what effect that will have on the resulting grain sample. In an arc, one is somewhat restricted in the materials that can be used and in the gas present during nucleation. Furthermore, one needs to worry about collection techniques that don't affect the sample.

Ground particles may be altered by the pressure used for the grinding and by contamination by the "mortar and pestle." Some of these concerns have been removed by the use of fluid air mills, where the "grinding" is accomplished by high speed impacts of grains with other grains in an inert gas flow inside a contained space, such as in a Trost Fluid Air Mill. The nature of the flow tends to avoid abrading the walls, as the fluid moves fastest at some distance away from the walls. Contamination is at a minimum, as the grinding is done by the material itself. The temperature is usually controlled by the temperature of the gas, and thus heating is minimized. However, it is difficult to collect the samples without the grains contacting room air (with the potential for chemical changes such as oxidation) and forming aggregates, although IDPs (and thus cometary grains by analogy) seem to be found in aggregates also; thus, this may actually be a positive aspect of the technique. One alternative sample production technique which attempts to minimize aggregation and thus determine the properties of separated grains is matrix isolation, which is discussed in Section 3.3.

Once the dust has been created by the technique of choice, the spectral dependence of emissivity (absorptivity) needs to be obtained by transmission or emission techniques. Although alluded to above, it will flesh out the example here to note specifically that a comparison of transmission and emission experiments has shown that using only the transmission through pressed KBr pellets containing ground samples will result in wavelength

shifts of the features (due to the refractive index of the pellet), as well as the inclusion of a strong scattering component near the edges of resonances which is inseparable from the absorptivity (emissivity). Allowing the dust to settle onto an already polished KBr window can alleviate the shift effect. However, one can only remove the scattering effect by measuring the emissivity directly, as discussed above.

In short, each method produces scientifically valuable samples worthy of study, but one must constantly be asking what effects may be attributable to the preparation and measurement techniques as opposed to the sample itself. In this example, the grains produced by the laser vaporization very strongly resemble IDPs in size, form, and amorphous nature, suggesting that, although they form faster than grains would in an astronomical environment, perhaps they do not form in a very different way, and we may use these results to further our understanding of the composition and structure of cosmic grains.

3.2 Hot Flow Grain Production

Another promising approach to the formation of cosmic grain analogues which is still under development involves the flow of gases through a series of furnaces resulting in nucleation and condensation of grains which can then be measured spectroscopically in situ. This technique is being pursued by, among others, Donn's group at Goddard and Arnold's group at the University of California at San Diego. In several respects these experiments will approximate the formation of grains in a proto- solar nebula or circumstellar shell. It will even be possible to add UV irradiation of the grains at a later time.

3.3 Organics and Low Temperature Volatiles

All of these techniques have been related to the grains known to be heated to, typically, over 300 K, and thus ignore the issue of the composition of the cometary nucleus where we believe ices play a predominant role. Based on cosmic abundance arguments, airborne measurements of water vapor in the coma, and now satellite fly-by experiments measuring the gas composition in situ, we now have strong support for the long-held belief that ices make up the major portion of the nucleus, with a significant dose of organic materials to help lower the albedo to less than 10%, perhaps less than 5%. This suggests that work on organics and ices will be critical to the success of future comet missions and our further understanding of comets, and that we should address sample preparations of this type here.

Chyba and Sagan (this meeting and 1987) and Khare, Sagan, Thompson, *et al.* (Sagan and Khare 1979, and Khare *et al.* 1987) have been experimenting with organic samples created under solar system-like conditions. These experiments have resulted in ice residues after irradiation and tholins created in a spark or UV-enriched environment which are promising analogues for cometary nuclear material. In particular, their fit to the $3.4/3.5\mu m$ features in the spectrum of Comet Halley with their lab data on a methane ice-clathrate residue are quite good, and we look forward to the results of follow-on studies. Based on cosmic abundances, one would expect to find methane ice in comets, but it has not been seen so far. If the reaction products in methane clathrates are truly responsible for the observed $3.4/3.5\mu m$ features, it would neatly explain the absence of the expected pure methane ice.

Unidentified IR emission features (UIR bands) are seen in many different astronomical objects at 3.3, 6.2, 7.7, 8.6, and $11.3\mu m$. It has recently been proposed that they may be carried by free, molecule-sized, polycyclic aromatic hydrocarbons (PAHs). As a class, PAHs are complex, planar, molecules made up of fused benzene rings which contain 20 to 50 carbon atoms and are extremely stable. Furthermore, model calculations suggest that these species, if present, would be as common as the most abundant, but far simpler polyatomic molecule, NH_3. Alternative explanations include hydrogenated carbon-rich molecules or very small grains (molecular clusters) which are heated to high temperatures by absorption of a UV photon. The excess $12\mu m$ flux correlated with galactic infrared

cirrus discovered with IRAS suggests the presence of a significant population of very small grains which are heated to high temperatures. Whatever the ultimate identification, in view of the ubiquity of the UIR bands in both galactic and extra-galactic sources, and the proposed link between interstellar and cometary dust particles, we expect this to be an important avenue of research in coming years.

In particular, there is some evidence for a weak 3.29μm feature in the spectrum of Halley, along with the stronger 3.36μm feature (the opposite of the situation in the spectra of most extra-solar system objects). This emphasizes our need to understand the emission mechanism in order to interpret correctly the spectra as we try to identify the composition and physical nature of the grains. Several proposed explanations for the 3.36μm feature are discussed in Chapter 3 of this report. Further laboratory tests of the viability of a fluorescence mechanism need to be conducted.

This new hypothesis of a previously unrecognized, but potentially very abundant component of the interstellar medium has important ramifications in many areas of astrophysics, and comets may eventually be our "laboratory" in which to test our models. For example, since the PAHs complexity and abundance would indicate a unique chemical history, not associated with the generally accepted ion-molecule interstellar chemistry models, they may well be the molecular progenitors of the larger carbonaceous dust grains (soot) which provide continuum emission and absorption in the infrared spectra of numerous astronomical sources. If this is the case, interstellar carbon particles may have PAHs in them, and if comets are related to interstellar grains, we would expect cometary "ices" to contain PAHs or PAH clusters.

Testing of the PAH/hydgrogenated carbon/molecular cluster hypotheses and their impact on the larger astrophysical picture is severely hampered, however, by a general lack of knowledge of the physical and chemical properties of such grains in the forms they are likely to be in in space: ions, dehydrogenated radicals and free neutral species. Their spectroscopic properties are extremely important to know since virtually all observational data pertaining to this problem are spectroscopic in nature. At Goddard, the absorption, emission, and fluorescence spectra of PAHs are being measured, as well as those of amorphous hydrocarbons, by several techniques.

The NASA-Ames group is also undertaking a program to fill some of this gap by using another common preparation technique not yet discussed here, that of matrix isolation (see, e.g., Moskovits and Ozin 1976, Gole and Stwalley 1982, and Meyer 1971). In this approach, the species of interest is isolated by suspension in a frozen, solid, inert matrix at about 10 K. This has the advantage of maintaining the grains as separate entities (helping to prevent clumping and coagulation), but raises the question of how the interaction between the grains and the matrix may affect the observed spectrum.

Once the matrix, in this case containing PAHs, has been prepared, UV, visible, and IR absorption spectra are measured. Subsequently, exposure to a UV radiation field mimicking the solar or interstellar field, as appropriate, can produce ionized or partially dehydrogenated PAHs. The spectra of these species can then be measured. In addition to the spectroscopic studies of individual PAHs, the Ames group will also be focusing on the properties of small carbon clusters (20-30 A in diameter) built up from PAHs. The laboratory data will then be used in theoretical modeling of UV-pumped IR fluorescence of PAHs and small amorphous carbon (soot) particles, and the possible application to understanding interstellar grains.

The pertinence to cometary grains will depend on further spectroscopic observation of comets at the wavelengths of the UIR bands; there is a possibility that the 11.3μm feature was seen in Halley (Campins, this meeting). In addition, as the molecules will emit differently when in a solid than when in a "gas" phase, further analysis of interplanetary dust particles and the results of a comet rendezvous will be needed before we can fully relate cometary and interstellar grains.

4.0 GRAIN PROCESSING

The section above treated the various ways one can create dust or grain samples in the lab which we believe simulate cosmic dust. However, as has already been mentioned above in passing, the astronomical grain is not created in the form in which it will live out its life; numerous forces act on a grain to alter it, including annealing, the passage of shock fronts which can actually cause vaporization and recondensation, the action of strong UV fields resulting in photolysis products and chemical reactions requiring an excitation energy suddenly becoming possible, sputtering by cosmic rays and ions and impacts among grains in denser environments, such as molecular clouds, and the addition of mantles through gas-grain collisions or hydration through grain contact with hydrogen and oxygen (or even water molecules) in the dark, cold, interior of these same dense clouds. As a result, laboratory simulations are not complete without addressing the effects of grain processing. Some grains, such as large silicate grains, may be strong enough to resist major change, and certainly several attempts to model warm interstellar/circumstellar dust with the Trapezium profile have met with success. However, the cometary environment shares with the dense, cold molecular clouds the strong probability that ices play a major role in determining the chemistry and physics of the solid phase, and in some instances the gas as well, and thus it is important to address processing of icy grains in particular.

We know from the measures of albedos that the surfaces of asteroids, the comae of several comets, and now the nucleus of Halley have remarkably low albedos, far too low to be ice as we are accustomed to seeing it. This suggests that contamination of the ice by dark material or processing of the ice by the environment is responsible for the dark appearance of the ice and that lab experiments to reproduce these low albedos are essential to our understanding of comets. Several groups have pursued and are continuing to conduct such experiments; these include the Leiden effort, Sagan and Khare's work, and, as noted below, the Ames effort.

4.1 Hydration

Some of the effects of hydration have been studied for silicates by, for example, Knacke and Kratschmer (1980) and Hecht *et al.* (1986), and for a variety of minerals which might have astronomical importance by Russell (1978). In each instance, spectral structure related to the amount of water of hydration could be reproducibly added to or removed from the spectrum by exposure to saturated water vapor or heat in a vacuum, respectively. Thus, the spectral shape, especially in the 5 to 8μm region, is a fine diagnostic of the amount of hydration. Currently, additional studies on the effects of hydration for amorphous grains are underway at Goddard (Nuth et al. 1985).

4.2 Thermal Processing

The studies of amorphous vs. crystalline silicates (Donn *et al.* 1970, Day 1976a, Nuth and Donn 1983a and 1984, and Stephens and Russell 1979) have shown that the temperature history of the grain can be quite well assessed by the degree of structure present in the 10μm spectra of (optically thin) silicate particles. Stephens was able to take amorphous olivine-composition glassy grains whose spectra matched the 10 and 20μm interstellar features well, heat them up to temperatures in the 500 - 700 K range and recover the same spectral shape as seen for the original (crystalline) olivine sample. Thus, if a comet, like Halley, is observed to have a double-peaked structure in its 10μm spectrum (Chapter 1), it is strong evidence for annealing of the cometary grains.

This is consistent with our picture of Halley material as having been heavily processed by multiple returns through the solar system, with repeated heating and cooling of the sticky, tough crust. Either heating portions of the crust to fairly high temperatures or irradiation processing (a combination of cosmic ray and UV-induced changes) in the surface could have altered the grain structure. The smooth spectra of the two first-time comets, Kohoutek and Wilson (Merrill 1974, Lynch *et al.* 1988 and abstract, this report), are also

consistent with this picture, as they would be expected to have unprocessed, primordial grains which would be amorphous in structure. On the other hand, we have no way of ruling out a different grain structure prior to the formation of Halley's Comet, or even precluding grain processing during the comet's formation.

Of course, we have a very limited data base of 10μm (much less 20μm) cometary spectroscopy, and not a lot more lab data on dust samples specifically created to be cometary dust analogues (Hecht *et al.* 1986, is one exception). Workshop participants felt vigorous lab programs could provide several types of data (e.g. spectral data to guide filter selection and plan spectroscopy experiments, and physical data on nuclear surface materials to plan for penetrator experiments) in support of the NASA comet missions to maximize their scientific return (see below).

5.0 LABORATORY GROUPS

As so little information is available concerning the properties of ices and grains which are relevant to the low temperature, vacuum, UV-irradiated environment of comets (much less the poorly understood formation environment of cometary grains), a substantial, continuing laboratory program is clearly necessary to further our understanding of comets as they are today, how they formed, and their relation to the particles in the interstellar medium. This is a particularly urgent need for NASA to support the two comet missions being planned (CRAF and comet sample return). For example, combined analyses of the water and dust production rates, in concert with models of the icy and refractory grain components and the physical structure of the comet nucleus would enhance our understanding of the design requirements for probe and sampling instrumentation. Chapter 5 enumerates the specific areas of study endorsed by the workshop participants which were felt to be necessary to meet these requirements and to carry our understanding of comets forward.

Sometimes an example of a successful laboratory effort can be a valuable planning aid for future work. Furthermore, we know of no existing guide to the many scattered current laboratory efforts, and thought it might be helpful at least to provide a rough guide to the existing group efforts which were discussed at the workshop. In this spirit, brief summaries thereof are listed below in addition to our example. This will not, then, be a complete list, presenting as it does distillations of workshop discussions; my apologies to those who may have been left out — it is no assessment of the quality of such a program.

A good example of an ongoing effort is found in the well thought out and well funded Laboratory Astrophysics program begun in Leiden in 1976, sponsored by the Physics and Astronomy Departments at Leiden University and charged with carrying out experiments of direct relevance to astrophysics. It is indicative of the level of support and long-term commitment workshop participants felt are necessary for significant progress in the field. In addition to a chaired professorship for overall management of the Laboratory (J. M. Greenberg) and two assistant professor, tenure-track positions (to develop and direct the lab and theoretical programs, respectively), the start-up group also included four graduate student/post-doctoral positions as well as a very substantial laboratory start-up budget.

Combining astrophysical theoretical expertise with an on-going experimental program has proven to be a very successful approach to tackling many difficult, interdisciplinary programs. The principal theme of the research has been to shed light on the physical and chemical properties of interstellar and cometary ices by carrying out laboratory studies of astronomical ice analogues. During the past 12 years, the group has studied the spectroscopic properties, from the vacuum ultraviolet through the infrared, of ices made up of simple materials as well as mixtures and the results of different types of processing experiments, such as deposition at various temperatures, annealing, UV irradiation effects, and temperature cycling effects. In recent years, the Leiden group has started to address questions concerning the role sulfur plays in determining the properties of ices. The number of astronomers from the U.S. who have participated in the Leiden group at the doctoral or

post-doctoral level is further testament to the importance of this research group. That no laboratory of comparable scope exists in the U.S. is not for lack of talent or interest, but for lack of dollars.

The Cornell group has also worked for many years on studies of mixtures relevant to solar system environments, including the study of tholins, ices, frosts, and methane clathrates (see abstracts in the Appendix, and Sagan and Khare 1979), and elemental sulfur in solid and liquid form in view of its prevalence in solar system bodies (Sasson, Wright, Arakawa, Khare, and Sagan 1985). In view of the substantial amount of dark, organic material measured in Halley by the satellite fly-by experiments,and the large fraction of the bulk of the nucleus believed to be icy in nature, these are also particularly relevant projects to the study of comets.

In 1984, a modest effort was begun at the NASA Ames Research Center to foster close collaboration between laboratory experimentalists, astronomical observers, and theoreticians. During the past few years, tremendous progress has been made in IR spectroscopy of comets and galactic sources either known or believed to have ices present, resulting in some tight constraints on the physical and chemical properties of such grain materials. The approach taken at Ames will be to carry out experiments on samples comprised of materials thought to be present on or in grains in the interstellar medium. For example, IR observations have shown that CH_4 is not a major ice constituent but that something like CH_3OH is likely to be present in astronomical ices. Thus, an experimental program focused on the photolytic and physical properties of interstellar ice analogues containing CH_3OH is under way. Ices containing polycyclic aromatic hydrocarbons (PAHs) will also be studied at Ames in view of the suggestion that they may be a ubiquitous component of the interstellar medium and that interstellar and cometary grains may well be related.

A major laboratory program in support of the study of interstellar grains from many directions has been going on at the Goddard Space Flight Center for many years. This program has included (but certainly has not been limited to) investigations of condensation processes (see Donn 1987, for a review of this subject with an excellent reference list), hydration effects in silicates, sputtering processes, temperature dependence of the spectral transmission of silicates (annealing, Donn *et al.* 1970, and Day 1974 and 1976a), and currently the effects of aggregates through fractal analysis (Donn 1987). Lab equipment for studying cluster beams has been evolving at GSFC for several years, and is presently quite productive (Donn et al. 1981). Also, experiments on the scattering by fractal aggregates using microwaves and scaled-up simulated grains are being enhanced in collaboration with the microwave facility, Space Astronomy Laboratory, University of Florida (Schuerman 1980), and P. Meakin, J. Stephens, B. Gustofson, and R. Wang.

Another microwave laboratory for investigating the scattering by irregular, inhomogeneous particles is located at the Ruhr University, Bochum, FRG. The Bochum group has been active for more than 15 years, particularly in the study of the polarization by irregular grains. They demonstrated the importance of "fluffy" structure in producing the observed polarization and backscattering by interplanetary dust (Giese *et al.* 1978.)

A continuation of the emissivity studies cited above (Russell 1978 and Stephens and Russell 1979) with new materials and sample preparation techniques is being continued at The Aerospace Corporation in collaboration with J. Stephens of Los Alamos. Funded primarily on in-house research money, and using instrumentation built in-house for IR astronomical observations from 2-14μm, this program has resulted in a promising match to some of the 6-8μm absorption features seen in dense, cool sources using straight forward silicate samples modified by hydration (Hecht *et al.* 1986). Additional samples with totally different but interesting compositions have been measured and the results are being prepared for publication.

There are a number of other groups around the world studying various aspects of grain processing and grain optical properties. Since 1981, the group at Lecce, Italy has been investigating the ultraviolet and infrared optical properties of various forms of amorphous

and hydrogenated carbon, PAHs, and SiC (Borghesi *et al.* 1985, Bussoletti *et al.* 1986). Sakata *et al.* (1984) have been investigating the properties of quenched carbonaceous composite (QCC). Several groups have been studying sputtering and effects of ion irradiation, including the AT&T Bell Labs laboratory group (Lanzerotti *et al.* 1984) and the group at Catania, Italy (Strazzulla 1985).

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